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CAUSES OF ANOMALOUS CRYSTAL GROWTH IN SINTERING CERAMICS AFTER FORMATION OF CLOSED PORES BEGAN

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The rapid growth of crystals after formation of closed pores begins in a sintered intermediate product is explained with the premises of the chemistry of crystals with defects and synergistics. The change in the structure of an infinite cluster of open pores as they are converted to closed pores decreases the concentration barrier of vacancies that prevent diffusion transfer through the boundaries and growth of the crystals. The nonisometric shape of the crystals and high rate of diffusion mass transfer promote the anomalous growth. The easy deformability of the boundaries of the crystals can lead to slight adjustment of their crystallographic orientations and joining of the crystals, which ensures their anomalously rapid growth.

In sintering of intermediate products made of highly disperse powders, crystals grow rapidly after the transition from open to closed pores begins [1]. This is usually observed after a decrease in the total porosity to approximately 10%. This process is especially intensive when nanopowders are used [2]. An abrupt change in the behavior of the samples was also observed in high-temperature creep after the porosity of the samples decreased to below 10% [3].

Anomalous sintering is observed in some types of ceramics, where some small crystals grow much larger. There are different explanations of this phenomenon [4]. The anomalous growth is due to the nonuniformity of the distribution of contaminants on the facets of the growing crystal, the presence of a liquid phase or solid phase with high diffusion mass transfer, porosity, the presence of denser regions in the intermediate product, strong anisotropy of the growth rates of different crystal facets, and a difference in their surface energy. Anisotropic crystals in the form of wafers usually grow rapidly in the direction parallel to their plane with the largest area and slowly in the perpendicular direction.

For some areas of application, for example, for increasing strength or thermal stability, anomalous growth can be useful, and larger crystals are specially added as seeds to stimulate anomalous growth in molding paste. In other cases, obtaining a finely crystalline ceramic is required, and anomalous crystal growth is harmful. Attempts are made to exclude it in fabrication of transparent ceramics, ferrites, and ferroelectric ceramics. In some types of ceramics, anomalous crystal growth is especially frequent, for example, in ceramics made of BaMO_3 ($M = \text{Ti, Zr}$) [5, 6].

We attempted to explain these phenomena from the positions of synergistics and chemistry of crystals with defects.

All processes in nature are irreversible and nonequilibrium [7]. Processes evolve in the order stability – instability – stability. Regions of unstable behavior of system, primarily bifurcation, are of special importance for technology [8]. In bifurcation, it is in principle impossible to predict the subsequent evolution of a system. An unstable state is not obligatorily bifurcation. We will use the general term “unstable state” in order to not substantiate the legitimacy of the term “bifurcation.” In multistability of a system, after an unstable state, it passes into one of the stable states which can differ strongly in properties. It is important that in the unstable state, the system acquires high sensitivity to all internal and external effects.

Exchange of energy, matter, and information with the environment forces the system (fired ceramic intermediate product) to create dissipative or accumulative structures. Accumulative structures store energy inside the system while dissipative structures dissipate it into the environment. This division is somewhat arbitrary, since both structures in a material can play the role of either a dissipative or an accumulative structure as a function of the conditions.

The goal of process engineers is to organize conduct of processes so that the system can be acted on in the region of the main unstable states that have a determining effect on the subsequent evolution of the system [9]. Internal or external controlling effects on the system, which must reliably surpass the level of uncontrollable effects (noise) can be used for this purpose. A high degree of nonequilibrium of a process in the region of an unstable state will increase uncontrollable fluctuations of the system (noise) and correspondingly the necessary controlling signals. For this reason, de-

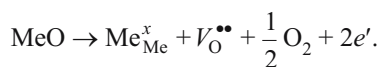
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creasing the degree of nonequilibrium of a process (its rate) in the region of the main unstable states is very effective and is frequently used [9].

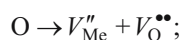
Structures created in a material in preceding stages of technology are internal controlling signals that affect the evolution of the structure of ceramics during firing. Crystals with a nonisometric shape (wafers, needles) easily form textures in molding of intermediate products — regions of their oriented position. The crystals are usually oriented by their maximum size (in which their growth rate is maximum) perpendicular to the applied force. This is in agreement with the LeChatelier – Braun principle, where a system reorganizes its structure so that an external effect is maximally reduced. This orientation simultaneously promotes contact of crystals with rapidly growing facets. The contaminants in synthesis of crystals by chemical methods are nonuniformly positioned on the growing facets. As a function of the type, these impurities can either accelerate or inhibit growth of the crystal facet. The surface energy of the crystal facets naturally changes, and their predisposition to anomalous growth can also be judged by this.

For effective diffusion mass transfer, cation and anion currents must be coordinated so that the overall electric current would be zero. The ratio of cation vacancies and anion vacancies (oxygen) must be close to the stoichiometric ratio of cations and anions in the oxide crystal, corrected for their mobility and driving force. Otherwise mass transfer will be limited by the concentration of the vacancies whose currents are lower than required to ensure overall zero electric current. This leads to perturbation of the electrical balance and inhibition of diffusion mass transfer due to the appearance of an electric field oriented so that it prevents diffusion flow (LeChatelier – Braun principle).

The concentration of oxygen vacancies increases at high temperatures in the near-surface layers of crystals (in the substance on the boundary of the crystals) in most oxides in the vacancy mechanism of diffusion due to the higher volatility of the oxygen anion in comparison to the metal cation [10]. As a result, oxygen vacancies $V_O^{\bullet\bullet}$ form in the oxygen sublattice, especially in the near-boundary layers of the crystal:



An increase in the concentration of oxygen vacancies $[V_O^{\bullet\bullet}]$ decreases the concentration of vacancies in the cationic sublattice $[V_{\text{Me}}'']$ according to the Schottky equation:



$$K_s = [V_{\text{Me}}''] [V_O^{\bullet\bullet}].$$

A decrease in the crystal size, which increases the volume of the near-surface regions, causes this process, i.e., it is intensified in highly disperse powders. Impurities, additives, the composition of the gas medium, and the presence of ten-

sile and compressive stress fields in the crystal have a large effect on the concentration of cation and anion vacancies.

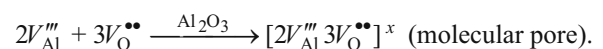
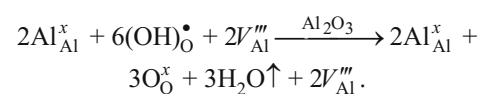
To accelerate diffusion mass transfer according to the vacancy mechanism, it is usually necessary to use additives that increase the concentration of cation vacancies. The concentration of primarily the most slowly diffusing cations should increase in complex oxides [10].

On the submicron level, a number of processes takes place in oxides when they are fired (in obtaining a dense ceramic) and they can be understood by using a quasichemical approach. Three main unstable states can be distinguished [9]. Sorbed atoms, primarily water, are removed, the fractality of the surface of the crystals decreases, stresses that arise in the intermediate product during its formation are removed, and binder is eliminated in the first state. A chip of the intermediate product becomes smoother. In the second state, basic plastic deformation of the intermediate product in shrinkage is observed. In the third state, open pores begin to be converted into closed pores. In some conditions, it can be possible to obtain a poreless and even a transparent ceramic.

Primary evaporation of oxygen at high temperatures causes a protective reaction of the system (LeChatelier – Braun principle) in the form of formation of a potential barrier on the boundary of the crystal due to a high concentration of oxygen vacancies there. The height of this concentration barrier is a function of the energy characteristics (fractality) of the given section of the surface, primarily the crystal size. The more rapidly and the larger number of oxygen anions that can escape from the boundary of the crystal, the higher the concentration barrier will be.

The barrier prevents further evaporation of oxygen and mass transfer through the boundary, i.e., crystal growth [9]. At the same time, the high concentration of vacancies causes loss of stability of the crystal structure of the substance on the boundary of the crystals and facilitates its plastic deformation. As stated above, in the vacancy mechanism of diffusion, mass transfer will be limited to cation vacancies.

Distortions of the crystal structure in the near-surface layer through which the diffusion path passes accelerate diffusion processes in it, aimed at perfecting it. In Al_2O_3 , the high concentration of vacancies (due to hydration and formation of $\text{Al}(\text{OH})_3$ on the surface) in the near-surface layer of the crystal causes the oxygen vacancies to join with cation vacancies, forming electroneutral associates — molecular pores. This can conditionally be written as:



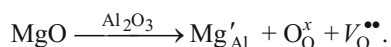
The concentration barrier for oxygen monovacancies probably does not affect $[2V_{\text{Al}}''' 3V_O^{\bullet\bullet}]^x$ associates. The associates surmount the concentration barrier, go out to the bound-

ary, which is a vacancy sink, and are annihilated in open pores during plastic strains during shrinkage. This process takes place intensively as long as the system of boundaries removes the molecular pores on the surface of the sample. The infinite cluster of open pores that joins the boundaries of the crystals with the surface of the intermediate product is most effective for these purposes. This could explain a well-known finding: in sintering, crystals almost do not grow before a certain minimum total porosity is attained (approximately 10%). The process of changing the structure (more accurately, its topology) of an infinite cluster of open pores before some of them begin to turn into closed pores corresponds to the third main unstable state [9].

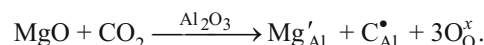
The infinite cluster of open pores in individual parts of the sintered intermediate product is transformed into regions isolated from the surface — closed pores. The formation of closed pores, combined with perfection of the near-surface layers of crystals and intercrystalline boundaries, complicates advantageous evaporation of oxygen from the near-surface layers of the crystals. This decreases the concentration of nonstoichiometric oxygen vacancies in the near-surface layer and the oxygen diffusion rate. As a result, in recrystallization of dense ceramics, it can become even less than for cations [11]. The concentration barrier for oxygen monovacancies on the surface of the crystals decreases so much that they begin to overcome it with cation vacancies in the necessary ratio, causing mass transfer and crystal growth. Moreover, the decrease in the shrinkage rate and correspondingly the intensity of plastic strains does not allow efficiently utilizing the mechanism of vacancy annihilation in open pores which is observed during rapid shrinkage of the sintered intermediate product (second main unstable state) [9]. The role of plastic strains is confirmed by the fact that it is frequently possible to make a denser ceramic from less dense intermediate products in which the plastic strain during shrinkage is greater when highly disperse powders are used.

If the degree of nonequilibrium of the process is such that the system cannot eliminate all molecular pores on the surface of the sample, the open pores play the role of sinks. Then crystal growth begins long before all of the molecular pores are removed, and it is not possible to manufacture poreless ceramics. The presence of pores in sintered ceramics is an example of the formation of accumulative structures in which energy is accumulated for formation of new surfaces.

Doping impurities that deter diffusion mass transfer are used to control the system in the region of the third unstable state with internal controlling signals. They slow the evolution of the infinite cluster of open pores to regions isolated from the surface (system of closed pores). In making transparent ceramics from corundum, doping impurities (MgO) that create oxygen vacancies and thus slow diffusion mass transfer were used:



In the vacancy mechanism of diffusion in oxides, an increase in the concentration of diffusion vacancies usually stimulates diffusion mass transfer and a decrease (for example, due to an increase in oxygen vacancies) inhibits it. In making transparent ceramics from corundum powder obtained by hydrolysis of aluminum oxide, the negative role of the carbon from alkoxide groups entering the structure was found. The carbon cations neutralized the effect of magnesium cations and decreased the concentration of oxygen vacancies, which did not allow obtaining transparent samples [12]. This could be attributed to the fact that carbon decreases the concentration of oxygen vacancies formed according to the previously cited reaction:



As a result, diffusion mass transfer was intensified, pores were captured by rapidly growing crystals, and the transparency of the ceramic was lost.

The use of highly volatile tungsten and molybdenum oxides of sintering dense mullite also probably caused preservation of the structure of the infinite cluster of open pores until high density of the intermediate product was attained (USSR Inventor's Certificate No. 1218629). The highly volatile oxides prevent conversion of open pores into closed pores.

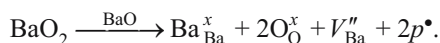
Superfast sintering, where the sample is placed in a furnace previously heated to the sintering temperature, is a very promising method. Dense finely crystalline samples can be obtained as a result of passing through all three main unstable states at a high degree of nonequilibrium. In very fast heating, the infinite cluster of open pores cannot change its structure due to conversion of some open pores into closed pores before the intermediate product attains high density, and this allows obtaining a highly dense, finely crystalline ceramic. Due to the thermal stresses that arise in the sintered intermediate product, this method is only applicable for fabricating small parts of simple shape, for example, small spheres for grinding. The use of microfiber heating, which ensures rapid volume heating of the intermediate product and decreases the temperature gradient, is more promising.

The textures that arise in the preceding stages of ceramics technology are prerequisites for anomalous growth of the crystals that form them. In the textures, the crystals are usually mutually oriented so that their most rapidly growing facets touch. In lamellar crystals, the probability of such mutual orientation is higher than in needle-shaped crystals. Moreover, the rapidly growing facets are enriched with impurities which can intensify diffusion mass transfer. They are also frequently the most rapidly growing due to the impurities, and growth can be ensured by nanoparticles and not by individual atoms. Particles in strong aggregates are especially strongly textured, which results in the well-known phenomenon where a large crystal is formed from a strong aggregate during sintering. Closed pores can either immediately be present in such aggregates or can primarily appear when there are no more closed pores in the remaining

sintered material. Crystals of nonisometric shape form textures whose density is higher than in untextured regions of the intermediate product.

In plastic deformation of intermediate products during sintering (shrinkage), conditions are created for additional mutual orientation of neighboring crystals and their contact by uniquely crystallographically oriented rapidly growing facets. The crystals can grow together with disappearance of the boundary between them. Anomalous rapid crystal growth is observed as a result, where a small number of large crystals is formed among (and due to) small crystals. Without the specially added seeds that play the role of an internal controlling signal in the evolution of the structure, the process would be probable in character. Everything would be determined by the successful mutual orientation of neighboring crystals. The conditions that favor such mutual orientation and diffusion mass transfer through the boundaries of the crystals will result in their anomalous growth. The presence of a liquid phase and vacancies (nonequilibrium and impurity) in the near-surface region of the crystals will significantly accelerate diffusion mass transfer.

Anomalous crystal growth is relatively frequently observed in sintering of BaMO_3 ceramics ($M = \text{Ti, Zr}$), which can be explained by quasichemical reactions. In synthesis of BaMO_3 , a deviation from stoichiometry (σ and γ) always appears in ordinary conditions; BaO , as a cation oxide with a higher diffusion coefficient, is concentrated on the surface of BaMO_3 crystals, while the internal regions of the crystals are a solid solution of MO_2 in BaMO_3 [13]. Since barium can form the peroxide BaO_2 , solid solutions of BaO_2 in BaO can arise in the substance on the boundary of the crystals according to the quasichemical reaction [14]:



In this case, while preserving the structure of an infinite cluster of open pores, a barrier of barium vacancies, and not of oxygen vacancies, in the substance at the boundary of the crystals will prevent mass transfer through the crystal boundary. Dynamic equilibrium is established through the infinite cluster of open pores between the environment, substance on the crystal boundary, and internal regions of the crystal.

Cubic barium oxide crystals are easily deformed at high temperatures due to their simple structure. Formation of a solid solution of BaO_2 in BaO should promote this process. This is in agreement with the high rates of high-temperature creep of alkaline-earth metal zirconates, including barium zirconate [15]. The easy deformability of the layer of substance on the crystal boundary covering BaMO_3 crystals is equivalent to a decrease in friction between crystals during shrinkage in sintering and in creep.

Changing the structure of an infinite cluster of open pores after some of them have been converted into closed pores changes the concentrations of vacancies in the layer of substance on the crystal boundary and in the internal regions of the crystal. In the layer of substance on the crystal bound-

ary, barium peroxide begins to lose oxygen and to transfer it to the nearest closed pores. The concentration of BaO_2 in BaO and correspondingly the barium vacancies decrease. The barrier that prevents diffusion mass transfer between the crystal boundary decreases and the crystals begin to grow.

The pressure of the gas (oxygen) in the closed pores, which increases as the barium peroxide decomposes, could be the cause of anomalously fast growth. For the crystals surrounding a pore, this is similar to hot molding. Due to the easy deformability of the crystal boundaries, this facilitates slight adjustment of the crystallographic orientations of neighboring crystals and joining of these crystals. Joining of the crystals can promote their anomalously rapid growth.

Diffusion mass transfer in a solid, which prepares the system for formation of large pores, requires time. For it to take place, the holding time must be increased or the temperature must be raised. For joining the crystals, their crystal lattices must be slightly adjusted by turning. The necessity of slight adjustment causes anomalous growth to not be observed everywhere, but only at sites where the situation was conducive to slight adjustment. Application of the pressure that arises in closed pores in decomposition of barium peroxide should promote such adjustment. This is in agreement with the experiments conducted in [6] in sintering of BaZrO_3 . It was shown that anomalous crystal growth began after the appearance of closed pores, which took place at temperatures above 1650°C or after holding at 1650°C for more than 2 h.

Anomalous crystal growth is thus caused by several interrelated factors. The nonisometric shape of the crystals, which is the consequence of the nature of the crystal itself or sorption of impurities on its growing facets, causes this. The nonisometric shape of crystals can arise both in synthesis of powder and in their growth during sintering. A nonisometric shape can also be formed during grinding due to the anisotropy of the strength properties of the different crystallographic planes of the crystal. Impurities, including those capable of diffusion mass transfer, are concentrated on the fastest growing facets. The process is accompanied by a change in the energy of the crystal facets.

During molding of articles, crystals with a nonisometric shape usually form textures in which conditions are created for contact of neighboring crystals by the rapidly growing facets. In appropriate orientation, the crystals grow together along such facets, ensuring their anomalously rapid growth. The easy deformability of the boundaries of the crystals promotes this process.

In oxide crystals with Schottky disordering, impurities forming cation vacancies accelerate diffusion mass transfer and plastic deformation. Growth of crystals and adjustment of their mutual orientation is caused by the high rate of diffusion transfer through the boundary of the crystals, including due to the presence of a liquid phase and the corresponding impurities. Such conditions arise after the structure of the infinite cluster of open pores changes when some of them are converted into closed pores, where the concentration barrier

of vacancies that prevent diffusion mass transfer through the crystal boundary decreases.

In sintering of complex BaMO_3 oxides ($M = \text{Ti}, \text{Zr}$), such a barrier can form barium vacancies due to the appearance of a solid solution of BaO_2 in BaO on the crystal boundaries. The anomalous crystal growth observed in sintering of BaMO_3 is due to the ease of deformation of the substance on the crystal boundary enriched with a solid solution of BaO_2 in BaO and the pressure in the closed pores caused by the oxygen formed in decomposition of BaO_2 . The easy deformability of the crystal boundaries leads to adjustment of their crystallographic orientations and joining of the crystals, which promotes their anomalous rapid growth.

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